Hindawi
International Journal of Chemical Engineering
Volume 2021, Article ID 9640918, 11 pages
https://doi.org/10.1155/2021/9640918

Research Article

Comparison of the Efficiency of Ultraviolet/Zinc Oxide (UV/ZnO) and Ozone/Zinc Oxide (O_3/ZnO) Techniques as Advanced Oxidation Processes in the Removal of Trimethoprim from Aqueous Solutions

Moayede Taie,[1] **Abdolmajid Fadaei**,[2] **Mehraban Sadeghi**,[2] **Sara Hemati**,[3] **and Gashtasb Mardani**[2]

[1]*Students' Research Committee, Research Center, Shahrekord University of Medical Sciences, Shahrekord, Iran*
[2]*Department of Environmental Health Engineering, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran*
[3]*Ph.D Student of Environmental Health Engineering, Department of Environmental Health Engineering, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran*

Correspondence should be addressed to Abdolmajid Fadaei; ali2fadae@yahoo.com

Received 14 April 2021; Revised 30 May 2021; Accepted 10 June 2021; Published 18 June 2021

Academic Editor: Sébastien Déon

Nowadays, advanced oxidation processes, particularly photocatalyst process and catalytic ozonation by ZnO nanoparticles, are the most efficient method of eliminating pharmaceuticals. The purpose of this study was to compare the efficiency of ultraviolet/zinc oxide (UV/ZnO) and ozone/zinc oxide (O_3/ZnO) techniques as advanced oxidation processes in the removal of trimethoprim (TMP) from aqueous solutions. The process consisted of 0.6 g/L of ozone (O_3), pH = 7.5 ± 0.5, TMP with a concentration of 0.5–5 mg/L, ZnO with a dose of 50–500 mg/L, 5–30 min reaction time, and 30–180 min contact time with UV radiation (6 W, 256 nm) in a continuous reactor. The high removal efficiency was achieved after 25 minutes when ZnO is used in 1 mg/L TMP under an operational condition at pH 7.5. When the concentration of the pollutant increased from 0.5 to 1, the average removal efficiency increased from 78% to 94%, and then, it remained almost constant. An increase in the reaction time from 5 to 25 minutes will cause the average elimination to increase from 84% to 94%. The results showed that the efficiency of O_3/ZnO process in the removal of TMP was 94%, while the removal efficiency of UV/ZnO process was 91%. The findings exhibited that the kinetic study followed the second-order kinetics, both processes. With regard to the results, the photocatalyst process and catalytic ozonation by ZnO nanoparticles can make acceptable levels for an efficient posttreatment. Finally, this combined system is proven to be a technically effective method for treating antibiotic contaminants.

1. Introduction

Today, water crisis throughout the world is evident. Therefore, reusing the drinking water is very important. One of the challenges related to water reuse is the removal of emerging contaminants (e.g., pharmaceuticals, personal care products) [1]. Antibiotics, which are one of the biggest groups of drugs, principally enter water sources by discharging from pharmaceutical industries and hospitals and urban wastewater effluents [2]. The accumulation and persistence of antibiotics in the environment can cause a potential hazard to the ecosystems. Actually, some of these materials are genotoxic and mutagenic and cause cancer [3]. Long-term exposure to low doses of antibiotics leads to the selective amplification of resistant bacteria, which could shift to other strains [4]. Trimethoprim has been reported to cause disorders in human health and environment (ecotoxicological, chronic ecotoxicity), modifying the breeding of animals and plants [5].

Trimethoprim (TMP) has been reported as one of the antibiotics currently detected in urban wastewaters and

surface waters [1]. This antibiotic concentration in surface waters and effluents was observed up to several hundred ng/L [6]. Concerns about trimethoprim are related to the potential for creating drug resistance [7] because of the widespread use in the treatment of infections in the upper respiratory tract and lower urinary tract and for kidney, gastrointestinal, and other bacterial infections since 1968. It is also used for prophylaxis and treating veterinary infections [8]. It is considered that trimethoprim is highly water soluble and provides low sorption to the sludge and easily enters and accumulates in aquatic resources [5]. The elimination of trimethoprim with the treatment of flocculation, adsorption, and oxidation showed different trends and had an efficiency of 10, 50, and lower than 90 percent, respectively [6]. TMP is the white powder that has high solubility in water [6], and its structure is illustrated [9] in Figure 1. Most of the currently used wastewater treatment techniques are not effective in removing these compounds completely [4]. For instance, ozonation was found to be effective for the removal of TMP in the drinking water treatment process [10]. Additionally, photocatalytic processes that are based on absorption of light for generation of active radicals have become an alternative for water clarification mechanism, leading to mineralization of organic compounds [11]. Six intermediates were identified during the photocatalytic decomposition of TMP. The exocyclic amino groups of the diaminopyridine ring and bridging methylene group are the potential active reaction sites in the TMP molecule [12]. Advanced oxidation processes (AOPs) have been shown to have a high efficiency in the elimination of various organic contaminants from drinking water and wastewater [1]. It is evident that research has recently been directed toward the application of AOPs due to their high performance in the decomposition of the organic matter [13]. Among various AOPs, ozonation was employed as one of the most popular AOPs. Ozonation has been traditionally employed in drinking water treatment for odor and taste control and disinfection, and for wastewater disinfection. Today, advanced oxidation processes for the elimination of pharmaceuticals in waters with emphasis on the use of catalysts have begun to enhance [14]. Instances of heterogeneous catalysts used in the advanced oxidation processes can be metal oxides such as ZnO and TiO_2 that are inexpensive, commercially available in various crystalline forms and particle characteristics, nontoxic, and photochemically stable [15]. TiO_2 and ZnO semiconductors are the most effective. ZnO has a wide band gap with an energy gap (EG) of about 3.3 eV. As a photocatalyst, ZnO has some important advantages such as low price and high photocatalytic activity (sometimes, activity bigger than TiO_2). The biggest advantage of ZnO is that it absorbs a larger fraction of the UV spectrum, compared with TiO_2 [16]. Unfortunately, these process measures have their own disadvantages like the difficulty in reusability of the adsorbent, the formation of degradation by-products, poor stability, high cost, and lack of practicality [17].

In this work, we compared the following two techniques used for trimethoprim degradation: ozone/zinc oxide (UV/ZnO) and ozone/zinc oxide (O_3/ZnO). The objective of this study is to investigate and compare the efficiency of ultraviolet/zinc oxide (UV/ZnO) and ozone/zinc oxide (O_3/ZnO) techniques as advanced oxidation processes in the removal of trimethoprim from aqueous solutions. The effects of ozone concentration, TMP concentration, ZnO dose, and residence time on removal efficiency were also explored.

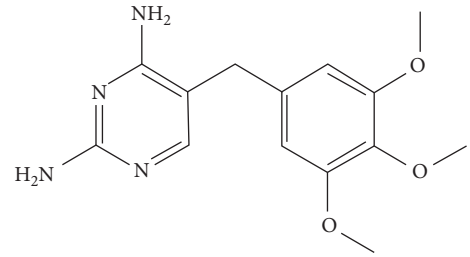

Figure 1: Trimethoprim structure.

2. Materials and Methods

2.1. Chemicals. TMP (standard, >98%) was purchased from Sigma-Aldrich with CAS number: 738-70-5. HPLC-grade methanol and ACN were supplied by Merck (Germany). A Milli-Q ultrapure water system (USA) was used to obtain HPLC-grade water. NaOH and H_2SO_4 were used as pH adjustment chemicals. ZnO (99% purity; Merck) was used for all experiments as received. Zinc oxide nanoparticles with 99% purity, 10–30 nm particle size, 20–60 m^2/g special level, nearly spherical, and milky white were used. ZnO was provided from Isfahan Science and Technology Town in Isfahan. Figure 2 illustrates the SEM of ZnO nanoparticles. *X*-ray diffraction (XRD) (Siemens D5000; Germany) was used to investigate the crystalline phase and solid structure of the ZnO nanoparticles (at 200 keV).

2.2. Experiments. Stock solutions were prepared in ultrapure water by constant stirring over 30 min by ultrasonic batch [18]. The concentration of TMP in the stock solution was 1000 mg/L [6]. In this study, several parameters were examined including catalyst doses (5, 250, and 500 mg/L) and concentrations of TMP (0.5, 1, and 5 mg/L) in a synthetic water model and contact time in order to investigate the influence of these parameters on the removal process [6]. Before reaction, the heterogeneous mixture was equilibrated for 15 min. Its pH value was maintained at 7.5 ± 0.5, and the reaction temperature was maintained at $25 \pm 0.5^{\circ}$C. Continuous experiments were performed in a glass cylinder with a height of 75 cm and a capacity of 11 L. The solution was circulated through a peristatic pump. Ozone dose was set on 0.6 mg/L. The ozone was generated from pure oxygen (>99.99%) using an ozone generator (Model OZ1-BTU; Ozotech, CA, USA), which was calibrated by an iodometry method [19] as in

$$O_3 \frac{\text{mg}}{\text{min}} = \frac{(A + B) \times N \times 24}{T\,(\text{min})}, \quad (1)$$

where A: mL of thiosulfate consumed in the first gas, B: mL of thiosulfate consumed in the second gas, T: ozonation time in minutes, and N: normality of sodium thiosulfate.

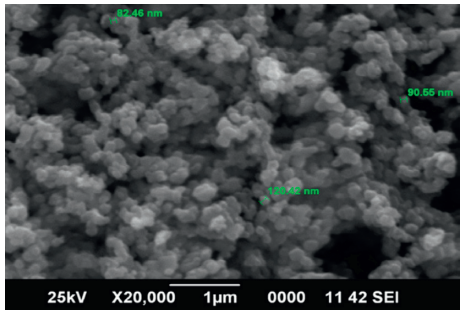

Figure 2: The SEM image of ZnO nanoparticles.

Ozone flow was transferred from a Venturi tube in the drift pump and was injected into the solution from the sintered diffuser for the maximum distribution and dissolution of gaseous ozone [20, 21]. The ozone contact time ranged from 5 to 30 min. Aliquots of samples were taken at predetermined time intervals (5, 10, 15, 20, 25, and 30 min) [18]. The semicontinuous photoreactor consisted of a vertical reactor with a total volume of 1 L, a UV lamp, and a magnetic stirrer in safety pilot. The source of radiation was a low-pressure mercury lamp (6 W) with a wavelength of 254 nm and a quartz glass tube, made by Arda France [22]. The suspension was continuously stirred using a magnetic stirrer. Subsequently, the solution was irradiated for 180 min. Aliquots of samples were taken at predetermined time intervals (30, 60, 90, 120, 150, and 180 min) [18].

2.3. Analysis. Solid-phase extraction using Oasis HLB cartridges (200 mg) was applied to samples to reduce the salt content in the matrix, before the chromatographic analysis. Cartridges were conditioned with 4 mL of methanol and 3 mL of water and loaded with a 50 mL of the samples. The cartridges were washed with 5 mL of Milli-Q water and then eluted with two aliquots of 5 mL of methanol. Before injection, extracts were diluted with 90 : 10 (H_2O/methanol) to recover the initial concentration [23].

2.4. Analytical Equipment and Methods. The concentration of TMP was monitored by HPLC (series1200; Agilent Technologies), equipped with C18 analytical columns (150 mm × 4.6 mm, 5 μm), used in isocratic mode (1 mL/min) with a FID detector. The mobile phase included methanol and water (10/90 V/V) with a flow rate of 1 mL/min. The mineralization content of TMP was determined on the basis of the TOC measurements. TOC measurements were performed by using a total organic carbon analyzer (Shimadzu TOC-VCSH). The ultraviolet spectrophotometric screening method (Shimadzu 1700; Japan) was used to measure nitrate and ammonium ions during the photodegradation of TMP.

2.5. Precision and Accuracy. All reagents were obtained from Sigma-Aldrich and Merck. Net purification water was used for purification of samples and standards during the study. All glass and plastic containers were washed with 10% HNO_3 overnight and then washed with deionized water to minimize contamination. The limit of detection (LOD) for TMP was 0.01 μg/L. The concentration of the TMP was recorded as zero if it was lower than the limit of detection. For study method validation, the TMP concentration was tested in spiked deionized water.

2.6. Ozone Decomposition. The residual ozone concentration in samples was determined by spectrophotometry using the indigo method [24] by equation (2). The concentration of gaseous ozone was determined by iodometry using potassium iodide solutions, and the residual ozone concentration was determined in the gas phase. The amount of ozone decomposition was defined as the difference between the initially applied ozone dose and the sum of the residual ozone doses in the water and gas [24]:

$$\text{ozone concentration in } \frac{\text{mg O}_3}{\text{l}} / = \frac{\triangle A \,.\, 100}{f \,.\, b \,.\, V}, \qquad (2)$$

where $\triangle A$ = difference in absorbance between sample and blank, b = path length of the cuvette in cm, V = volume of the sample added in mL (normally 90 mL), and $f = 0.42$.

3. Results and Discussion

3.1. Preliminary Experiments with TMP. The observations showed that ZnO nanopowders alone did not degrade TMP, but removal efficiency of ozonation alone was shown to be 89%. However, O3/ZnO removed about 99% of TMP within 30 min of reaction time (Figure 3). The decomposition of TMP is very high in the presence of the ZnO catalyst, compared with when the catalyst was not used. Ozone is unstable in water. Depending on the water quality, the half-life of ozone is in the range of seconds to minutes. The principal secondary oxidant formed from ozone decomposition in water is the OH radical. The stability of ozone largely depends on the water matrix, especially its pH, the type and content of natural organic matter (NOM), and its alkalinity. In the experiments, the synthetic water model was in Milli-Q water and pH value was maintained at 7.5 ± 0.5 [25].

It seems that ZnO nanopowder alone did not degrade TMP (0.5 mg/L), and the degradation of antibiotics by UV irradiation alone has removal efficiency of about 27% (Figure 4) As well as, the UV/ZnO photocatalytic process removed about 91% of TRI within 180 min of irradiation. The present results agree with a number of various previous AOP studies that have the discussion on the removal of pollutants by the similar method. Advanced oxidation processes (AOPs) through the production of hydroxyl radicals (HO•) have been considered to be very hopeful alternative techniques to water decontamination [13]. These experiments exhibited that both UV light and a photocatalyst, such as ZnO, were required for the effective removal of pollutants because the photocatalytic destruction of organic matters in solutions is started by photoexcitation of the semiconductor and after that formation of an electron-hole pair on the surface of catalyst [26]. Similarly, for a study on C.I. Acid Orange 7 and diazinon, photocatalyst degradation

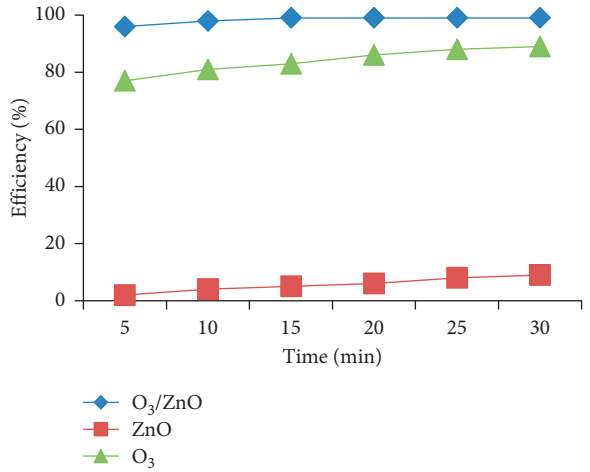

FIGURE 3: TMP removal by different treatment processes (ZnO = 500 mg/L).

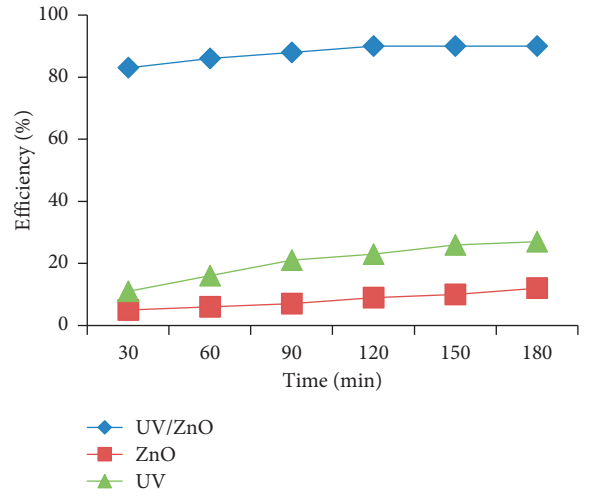

FIGURE 4: TMP removal by different treatment processes (TMP = 0.5 mg/L) (P value = 0.032).

of TMP was negligible when ZnO nanopowder and UV light were used on their own [26].

In the UV/ZnO photocatalyst process, zinc oxide when illuminated by photons having an energy level that surpasses their band gap vitality excites electrons (e^-) from the valence band to the conduction band, thus creating holes (h^+) in the valence band. The photogenerated valence band holes react with either water (H_2O) or hydroxyl ions (OH^-) adsorbed on the catalyst surface to create hydroxyl radicals (•OH), which are powerful oxidants and degrade TMP. The hydroxyl radical formation caused by radiation to the ZnO surface is shown in [27]

$$\mathrm{ZnO} + h \longrightarrow \mathrm{ZnO}\left(e^- + h^+\right), \tag{3}$$

$$h^+ + \mathrm{TMP} \longrightarrow \mathrm{TMP}^{0+} \longrightarrow \text{oxidation of the TMP}, \tag{4}$$

$$h^+ + \mathrm{H_2O} \longrightarrow \mathrm{H}^+ + \mathrm{OH}^0, \tag{5}$$

$$h^+ + \mathrm{OH}^- + \longrightarrow \mathrm{OH}^0. \tag{6}$$

The biggest advantage of ZnO is its ability to absorb a range of electromagnetic and photocatalytic capabilities under UVA radiation. In fact, ZnO is nontoxic with chemical stability at high temperatures and able to produce chemical oxidation [28].

3.2. Effect of the Catalyst Doses. Increasing the concentration of the catalyst has a slight effect on the increase of the removal average rate. Results of the comparison of the mean values of the removal efficiency in Figure 5 show that increasing the dose of the catalyst has achieved faster destruction rates and higher overall decomposition of TMP. Thus, the efficiency of removal was 87.49% when 50 mg/L of ZnO was used, whereas 90.4% was achieved by increasing the catalyst dose to 250 mg/L and 92.38% when 500 mg/L of catalyst was used. The catalytic ozonation process has two mechanisms: direct oxidation of pollutants by ozone molecules and indirect oxidation by hydroxyl radicals generated from the molecular ozone [29]. The increase of ZnO leads to the increase of the ozone decomposition rate and the increase of OH production, there upon the highest removal is achieved (Figure 4). Also, results of a similar study have shown that the high reactivity of hydroxyl radicals that were generated in high ZnO concentrations during the oxidation process effectively degraded TCP and thus confirms the findings [30]. Another study showed that the most effective TiO_2 dose was recognized as 100 mg/L in terms of TMP decomposition [12]. Another study showed that TiO_2 dose of 200 mg/L was most effective in terms of TMP decomposition [23]. Abellan et al. reported that degradation of SMX and TMP was improved when the TiO_2 concentration was increased up to 500 mg/L [31].

The observations showed the degradation of TMP increased with the enhancement of ZnO dosage (P value = 0.006) presumably due to the increase in •OH production. The most effective ZnO dose was recognized to be 500 mg/L in terms of TMP destruction (Figure 4). The efficiency increased slightly from 83.1% at ZnO dose of 50 mg/L to about 91% at 500 mg/L of ZnO. It has been conjectured there was no improvement with the further increase in the catalyst doses, probably. The results proved were similar to degradation of other contaminants (antibiotics, pesticides, and dyes), TMP removal is signally affected by catalyst dosage, and the photodegradation efficiency increases with an increase in ZnO dosage. However, at high dosage, the increase of the rate was decreased gradually. Previous studies compared the catalytic activity of ZnO and TiO_2 for the degradation of sulfamethazine and chloramphenicol respectively and reported that ZnO was slightly more effective than TiO_2 [14].

It can be seen that the destruction of antibiotics with the enhancement of ZnO concentration was probably due to the increment in OH generation. However, increasing ZnO

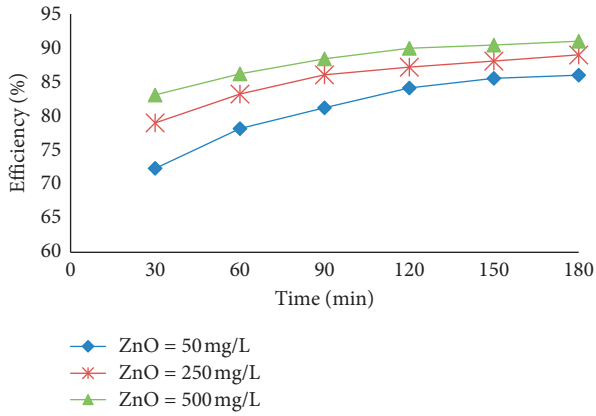

Figure 5: Effect of initial ZnO dose on degradation during treatment processes. UV: 6 W; TMP: 0.5 mg/L; and pH: 7.5 ± 0.5.

concentration above 500 mg/L did not deliver any critical change in antibiotics degradation. This may be due to diminishing UV light penetration as a consequence of an increase in turbidity and thus decreasing the photoactivated volume of the suspension [32]. In previous studies on other pollutants by expanding the initial ZnO dosage from 0.0 to 5.0 g/L, mineralization of amoxicillin, ampicillin, and cloxacillin and also degradation of C.I. Acid Orange 7 additionally expanded until reaching a certain level [26]. According to the previous investigations and our work, the increase in the amount of catalyst added increased the number of active sites on the photocatalytic surface, which thus expanded the number of hydroxyl and superoxide radicals. Also, after getting the optimal level of the photocatalyst, further expanding photocatalyst dosage does not increase removal efficiency [33]. Hence, after that, further catalyst loading does not influence the degradation significantly often. This observation can clarify as far as accessibility of active sites on the catalyst surface and the influx of UV light into the solution. The total active surface area increases with an increase in the catalyst dosage. At the same time, due to the increase in the turbidity of the solution, there is a reduction in UV light influx as a result of increased dispersion effect, and hence the photoactivated volume of the solution decreases. Furthermore, at high catalyst loading, it is hard to maintain the homogeneity of the solution due to particles agglomeration, which diminishes the quantity of active sites [26]. The photocorrosion of ZnO is complete at pH lower than 4 and at pH higher than 10, and no photocorrosion of ZnO takes place at pH = 7 [34]. Shankaraiah et al. reported that the UV/TiO_2 process removed 61 to 90% of norfloxacin [35]. Another study showed that TiO_2 photocatalysis was the most effective method for removing β-lactam antibiotics [36]. Aissani et al. indicated that the UV/TiO_2 process removed 41% of sulfamethazine (The combination of photocatalysis process [34].

One study indicated that a nanoparticle TiO_2-based photoelectrocatalytic process has high potential to be utilized as an appropriate treatment method for pharmaceutical effluents containing cefotaxime antibiotics [37]. One of the most important problems of this process is recycling of nanoparticles, which can be addressed by doping and codoping of metal oxide nanomaterials, immobilization of nanoparticles on appropriate matrices, and nano-based filters through the combination of clay/ZnO nanocomposites [38, 39].

3.3. Effect of Initial TMP Concentrations. The effect of the initial TMP concentration was an assessment. Figure 7 shows the rate of decomposition was greater for higher TMP concentrations. The catchment of ozone is greater in a more concentrated solution; obviously, ozone is in exposure with more pollutant molecules and more of trimethoprim antibiotic molecules are decomposed by ozone.

The results of the comparison of the mean values of the removal efficiency show that with increasing the initial concentration of TMP, the efficiency of removal has increased. Hence, the removal efficiency was 78.89% when the initial concentration of trimethoprim was 0.5 mg/L, and this amount increased to 94.06% for 1 mg/L TMP and was 96.88% when 5 mg/L of pollutant was used. Hence, for achieving high removal efficiency in a few minutes, it is better to use catalytic ozonation in a high concentration of contamination or the concentrated solution. The ozonation efficiency increases in higher concentrations of trimethoprim and zinc oxide. Passing through more concentrated solutions, ozone molecules are encountered with more pollutants. Hence, the catchment and consumption of the ozone solution are greater in more concentrated solutions and as a result, the direct oxidation of the pollutants occurs more by the ozone molecules. Shabani et al. [20] concluded the same in their research by using a new reactor system containing a centrifuge pump and a Venturi tube, and the capability of ozonation in the treatment of the leachate generated in the landfill indicated that efficiency is much greater in more concentrated leachates [20]. The effect of the initial TMP concentration was also been evaluated, and the results are shown in Figure 7. The rate of photodegradation was higher for lower TMP concentrations (P value = 0.006), which the reason for the interfering effect of turbidity, probably. This process has improved in lower TMP concentrations (more dilute solutions) because turbidity interferes with the UV irradiation. It took less than 120 min to break down the TMP compound if we want to save our economy and time [9]. As for dyes [33] and insecticides [26] in previous similar studies, the rate of degradation reduces with increasing initial concentration of a model solution. The level of photodegradation diminished with expanding the concentration of pollutants. Also, when the initial concentration is increased, more organic substances are adsorbed on the surface of ZnO. Along these lines, there are just a less number of active sites for adsorption of hydroxyl ions, so the production of hydroxyl radicals will be decreased. Furthermore, as the concentration of a pollutant solution increased, the photons get intercepted before they reach the catalyst surface; thus, the absorption of photons by the catalyst diminishes, and subsequently, the degradation percent is decreased [40–42].

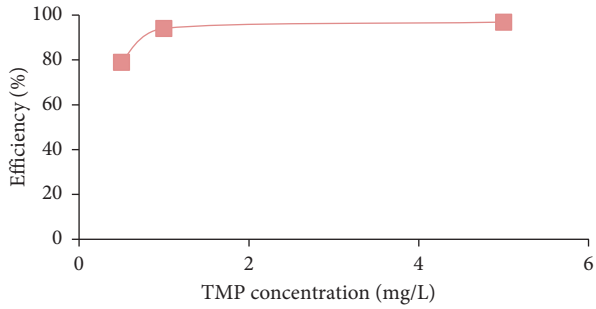

Figure 6: Effect of initial TMP concentrations on the UV/ZnO process.

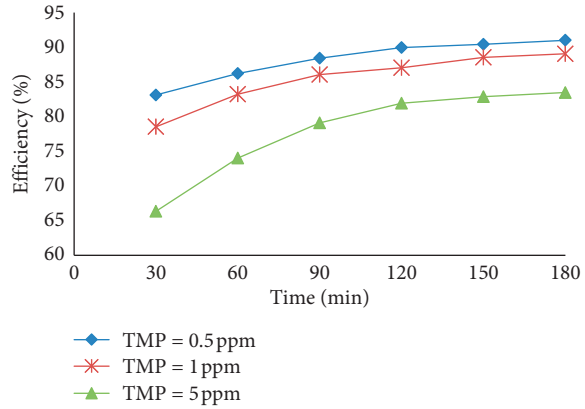

Figure 7: Effect of initial TMP concentrations on degradation during treatment processes. UV: 6 W; ZnO: 500 mg/L; and pH: 7.5 ± 0.5.

3.4. Effect of Reaction Time. In this study, the removal efficiency has increased over time. The results of the comparison of the mean values of removal efficiency in Figure 3 show that with increase in the time, due to a greater opportunity for contact of hydroxyl radicals and trimethoprim molecules, the removal efficiency increases from 84.63% in the first 5 minutes to 94.19% after 25 minutes. However, the slope of the curve decreased in the latter times, and finally, after 30 minutes, the efficiency of the elimination decreased to 92.94 percent. At 2 hours, the slope of the graph was higher than the remaining time. It was reduced after this 120 min, and the removal efficiency obtained was around the same removal efficiency obtained at 120 min. The rate of photodegradation increased slightly from 0 in the initial time to about 90% at 120 min when the initial TMP concentration was 0.5 mg/L and catalyst dose was 500 mg/L. Overall performance increases with increasing contact time. In a study by Adhami to evaluate the efficacy of the UV/ZnO photocatalytic process in removing antibiotic cefalexin from aqueous solutions, they increased the removal efficiency by increasing the contact time due to the production of hydroxyl radicals [43]. Another study showed that removal efficiency was increased with increasing contact time [44].

3.5. Kinetics Determining the Reaction. The decomposition rate of TMP was evaluated in the photocatalytic oxidation process. The photodegradation data of TMP show the second-order reaction rate in this experiment, and Figure 8 shows the photodegradation rate for TMP. Ct is the trimethoprim concentration at the desired time. $R^2 = 0.9675$ and $K = 0.0703$ (L/mg s). The O_3/ZnO process data of TMP are presented in Table 1. In a study by Elmolla and Chaudhuri, the degradation of amoxicillin, ampicillin, and cloxacillin antibiotics in aqueous solutions by the UV/ZnO photocatalytic process followed a pseudo-first-order kinetics [32].

3.6. Mineralization Studies. In order to study the mineralization of TMP, the TOC and concentrations of NO_3^- and NH_4^+ ions were measured. Table 2 shows that the TOC of the solution ($C_0 = 0.5$ mg/L, ZnO = 500 mg/L, and pH = 7.5) has decreased about 91% after 180 min. The reduction of TOC and the increase of ions' concentrations in the solution represent the mineralization of TMP solution. The measurement of UV absorption of TMP solution at 220 and 275 nm in the presence of HCl, as a reagent, enables rapid determination of nitrate. For determination of ammonium ions, a solution of TMP was prepared using different reagents such as $ZnSO_4$, NaOH, and Rochelle ($KNaC_4H4O_6.4H_2O$), and after 10 min, the intensity of absorbance peak was measured by a spectrophotometric method [45]. The results are shown in Table 3

3.7. Ozone Decomposition. The consumed ozone, outlet ozone, and residual ozone were measured at different concentrations of the catalyst and trimethoprim, and some of their results are shown in Figures 9 and 10. These graphs indicate that the increase in the initial concentration of trimethoprim has reduced the amount of ozone depleted from the reactor and increased the amount of soluble ozone and consumed ozone. Also, the increase in the catalyst dose has reduced the amount of ozone depleted from the reactor and slightly increased the amount of ozone and the ozone solution and consumed ozone. The transfer efficiency of ozone and the transferred dose are shown in Table 2. A negative sign indicates that the consuming ozone for 0.5 mg/L TMP is less than the outlet ozone. Using the ozone concentration average in the solution, the ozone concentration average in the outlet gas of reactor, and the consumed ozone concentration average, the transfer efficiency of ozone was calculated using equation (7). By measuring the average cumulative ozone depleted from the reactor and the average cumulative ozone consume, the transfused dose was calculated using [46]

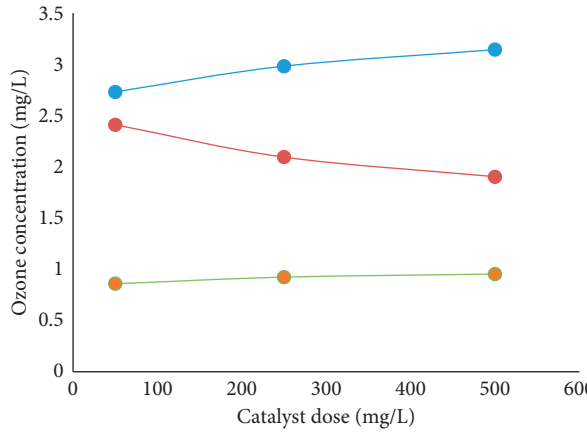

Figure 8: Effect of catalyst dose on ozone decomposition (TMP = 0.5 mg/L); •: consumed ozone, ◆: residual ozone, and ▲: outlet ozone.

Table 1: Summary of the kinetic analysis results of TMP removal for O_3/ZnO process.

Kinetics	K	R^2
Zero order	0.018 (mg/L s)	0.7553
First order	0.008 (L/s)	0.9000
Second order	0.041 (L/mg s)	**0.9720**

Table 2: TOC and ion measurements for degradation of trimethoprim using UV/ZnO process.

Time (min)	0	90	180
TOC	4.20	0.84	0.47
NO_3^- concentration (mg/L)	0.79	6.7	16.4
NH_4^+ concentration (mg/L)	0.04	1.3	3.29

Table 3: The transfer efficiency of ozone and transferred dose.

ZnO = 500 (mg/L)	ZnO = 250 (mg/L)	ZnO = 50 (mg/L)	TMP (mg/L)	
49.66	45.83	38.33	0.5	Transfer efficiency
−8.85	−15.61	−31.14	0.5	Transferred dose
69.33	64.5	57.66	1	Transfer efficiency
27.03	16.84	4.91	1	Transferred dose
84.33	83	80.83	5	Transfer efficiency
48.77	46.70	43.59	5	Transferred dose

*A negative sign indicates that the consuming ozone for 0.5 mg/L TMP is less than the outlet ozone.

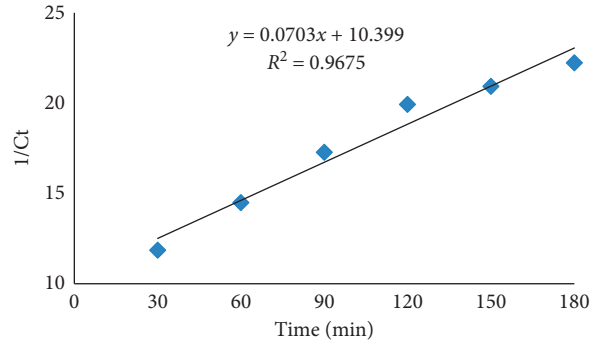

Figure 9: The second-order reaction rate in TMP photodegradation oxidation process.

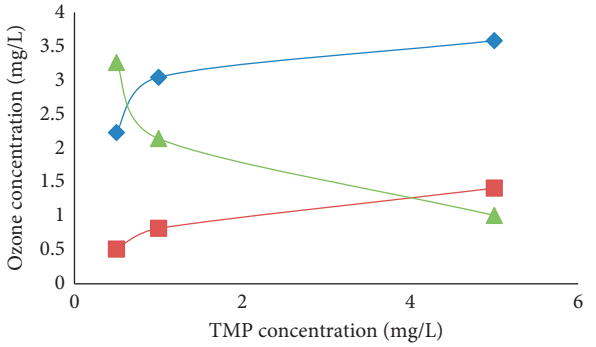

Figure 10: Effect of initial TMP concentrations on ozone decomposition (ZnO = 50 mg/L); •: consumed ozone, ◆: residual ozone, and ▲: outlet ozone.

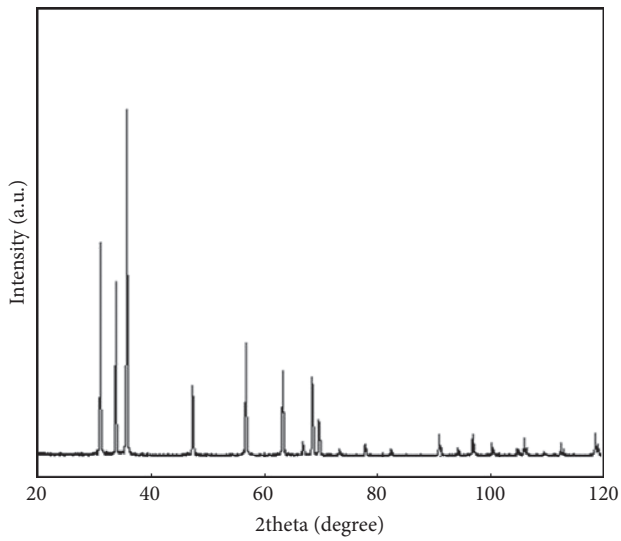

Figure 11: The *X*-ray diffraction (XRD) patterns of the ZnO nanoparticles.

$$(\%)\ \text{the transfer efficiency of ozone} = \frac{\text{inlet gas} - \text{gas outlet}}{\text{inlet gas}} \times 100, \tag{7}$$

$$\left(\frac{\text{mg}}{\text{L. min}}\right)\ \text{transferred dose} = \frac{(\text{mg/L min})\text{gas consumed} - (\text{mg/L min})\text{gas outlet}}{(l)\text{reactor volume}} \times (\text{min})\text{exa mination time}. \tag{8}$$

Ozone decomposition is a function of catalyst concentration, and with increasing the concentration, the rate of decomposition increases, especially at the early stages of the process. As already mentioned, it shows the catalytic role of decomposition of ozone and the formation of hydroxyl radicals [47]. Increasing the concentration of contaminants also increases the decomposition of ozone molecules because, in the more concentrated solution, the ozone molecule is more closely contacted with trimethoprim molecules. In addition to radical hydroxyl production, the reaction occurs between the ozone and the trimethoprim. Hence, we have high ozone consumption and more pollutant removal, while in the dilute solution, this direct reaction is less [48]. The results of transfer efficiency of ozone and transferred dose of ozone can be related to the type of the system used for ozonation. The system used in this research includes a Venturi tube with a peristaltic pump with return solution. Since, in this case, ozone is injected by pressure into the effluent after passing through the Venturi tube, and through a structure similar to a glass diffuser, the injection of the gas in this system makes the gas bubbles smaller and so the overall contact area of the gas bubbles with the liquid phase increases. Therefore, it can be expected that ozone decomposition and removal efficiency can be improved with increasing the solution concentration. Here, the effect of an increase in the initial concentration of antibiotics is greater than the increase in the catalyst dose [20, 46]. Similar research has shown that the ratio of ozone consumption to antibiotic degradation is low in the early minutes of the reaction in the ozonation process and gradually increases. However, high ozone consumption per unit of the pollutant can be related to the competition of trimethoprim with intermediates in combination with oxidizing agents. Perhaps, the other reason is to reduce the efficiency of the ozone molecules at the end of the process due to the reduced reaction rate of the carbonic acid produced [49].

3.8. Chemicals. The results of the SEM image showed that the Zn nanoparticle size in this study was less than 150 nm, and the SEM technique showed no impurity in the zinc oxide nanoparticle used in this study (Figure 2). X-ray diffraction (XRD) was conducted to characterize the structural properties of catalyst (characterization of constituent phases and crystalline size of nanoparticle) (Figure 11). The peaks of the XRD patterns of the ZnO nanoparticles are quite sharp, indicating the crystalline nature of the nanoparticles.

3.9. Comparison of O_3/ZnO and UV/ZnO Processes. The results indicated inefficient adsorption of TMP by ZnO alone (9%). In fact, the adsorption process was an inefficient treatment method to be used for the removal of TMP as an independent process (Figures 3 and 4). Totally, the adsorption process only transfers the contaminant from the liquid to the solid phase (adsorbent construction) and does not change its toxic character. According to the results, under similar conditions, including ZnO dose, concentration of TMP, and experiment location, the O_3/ZnO process showed greater removal efficiency than the UV/ZnO process (Figures 3 and 4). The optimal conditions for removal of TMP were 0.5 mg/L of TMP, 500 mg/L of ZnO dose, 0.6 g/L

Table 4: Comparison of removal efficiency of antibiotics in aqueous solution by advanced oxidation processes.

Antibiotic	Environment	Process	Operation conditions	Removal efficiency	Reference
Trimethoprim	Synthetic water model	UV/ZnO, O_3/ZnO	Ozonation rate = 0.6 g/L, ZnO = 500 mg/L, low-pressure UV (6 W, 254 nm)	91%, 94%	This study
Trimethoprim	Spiked STP effluent	O_3	0.1–0.3 mM O_3, pH = 7.2	85%	[50]
Trimethoprim and ciprofloxacin	2.5 mM phosphate buffer saline, pH = 7	O_3/H_2O_2/UV	O_3 = 0.1 mM H_2O_2 = 0.05–0.1 mM, medium pressure	>90%	[51]
Ciprofloxacin	Ultrapure water	UV/TiO_2	Dose catalyst (0.35 g/L), low-pressure UV	100% in 45 min	[52]
Metronidazole	Complex aqueous matrix	UV/TiO_2	TiO_2 = 1.5 g/L, UV light intensity = 6.5 mW cm^{-2}	88% in 30 min	[53]
Tetracycline	Deionized water	US/ ZnO + nanocomposite	ZnO/NC = 4.88 mg, US frequency and power 37 kHz and 256 W	87.6% in 45 min	[54]
Ciprofloxacin and trimethoprim	Ultrapure water	UV/O_3	2–20 mM O_3, medium-pressure polychromatic UV lamp	~100%	[51]
Ciprofloxacin	Synthetic and simulated wastewater samples	O_3/CaO_2	CaO_2 = 0.025 mg/L, temperature = 25°C, ozonation rate = 1 g/min	95.6% and 85.4%	[55]
Ciprofloxacin	Synthetic water model	O_3/UV/ZnO	Ozonation rate = 4 L/min, UV lamp 6 W and low pressure, ZnO = 0.3 g/L	96% in 30 min	[44]

of ozone concentration, and pH = 7.5. Under these conditions, removal efficiency of UV/ZnO and O_3/ZnO processes was obtained as 91% and 94%, respectively. The result obtained was found similar or even better than those reported by other authors (Table 4).

4. Conclusions

This study indicated that the presence of nano-ZnO with O_3 showed a significant increase in the degradation of TMP than with ozonation alone. There is a direct relationship between TMP concentration, ZnO concentration, and contact time with the removal efficiency. The increase of ZnO concentration from 0.5 to 500 mg/L will also lead to the increase of the ozone decomposition efficiency; therefore, production of OH increases, which leads to an increase in the degradation of antibiotics and removal efficiency in a short time.

Because the catchment and consumption of ozone in the more concentrated solution are much greater, ozone has exposure to more pollutants; therefore, ozonation efficiency has increased. Of course, type of the ozonation system and the structure of the pollutant are very influential in ozone transfer efficiency and doses and, subsequently, in the decomposition and consumption of ozone and removal of the contaminants. By UV irradiation alone, degradation of TMP concentrations was low, while the mineralization by UV/ZnO photooxidation occurred in over time. All results obtained from the present study clearly showed that ZnO concentration, TMP concentrations, and contact time played key operating factors in the removal of antibiotics. There is a direct relationship between ZnO dose and contact time with removal efficiency, while this is reverse for TMP concentration. Based on the findings, the removal efficiency of the O_3/ZnO process was higher than that of the UV/ZnO process. Therefore, this method is suitable for the removal of TMP because of its low cost, safety, and biocompatibility, and combination of UV/ZnO process with renewable energy sources in order to reduce both economic and environmental impacts is recommended.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors thank the Shahrekord University of Medical Sciences (grant number: 2757) for supporting this study.

References

[1] F. L. Rosario-Ortiz, E. C. Wert, and S. A. Snyder, "Evaluation of UV/H_2O_2 treatment for the oxidation of pharmaceuticals in wastewater," *Water Research*, vol. 44, no. 5, pp. 1440–1448, 2010.

[2] G. Z. Kyzas, J. Fu, N. K. Lazaridis, D. N. Bikiaris, and K. A. Matis, "New approaches on the removal of pharmaceuticals from wastewaters with adsorbent materials," *Journal of Molecular Liquids*, vol. 209, pp. 87–93, 2015.

[3] C. G. B. Brenner, C. A. Mallmann, D. R. Arsand, F. M. Mayer, and A. F. Martins, "Determination of sulfamethoxazole and trimethoprim and their metabolites in hospital effluent," *CLEAN—Soil, Air, Water*, vol. 39, no. 1, pp. 28–34, 2011.

[4] A. L. Batt, I. B. Bruce, and D. S. Aga, "Evaluating the vulnerability of surface waters to antibiotic contamination from varying wastewater treatment plant discharges," *Environmental Pollution*, vol. 142, no. 2, pp. 295–302, 2006.

[5] S. Oros-Ruiz, R. Zanella, and B. Prado, "Photocatalytic degradation of trimethoprim by metallic nanoparticles supported on TiO_2-P25," *Journal of Hazardous Materials*, vol. 263, pp. 28–35, 2013.

[6] D. Ho, S. Vigneswaran, H. H. Ngo et al., "Photocatalysis of trimethoprim (TRI) in water," *Sustainable Environment Research (Formerly J. Environmental Engineering and Management)*, vol. 21, no. 3, pp. 149–154, 2011.

[7] C. C. Ryan, D. T. Tan, and W. A. Arnold, "Direct and indirect photolysis of sulfamethoxazole and trimethoprim in wastewater treatment plant effluent," *Water Research*, vol. 45, no. 3, pp. 1280–1286, 2011.

[8] A. F. Martins, C. A. Mallmann, D. R. Arsand, F. M. Mayer, and C. G. B. Brenner, "Occurrence of the antimicrobials sulfamethoxazole and trimethoprim in hospital effluent and study of their degradation products after electrocoagulation," *CLEAN—Soil, Air, Water*, vol. 39, no. 1, pp. 21–27, 2011.

[9] J. N. Bhakta and Y. Munekage, "Degradation of antibiotics (trimethoprim and sulphamethoxazole) pollutants using UV and TiO_2 in aqueous medium," *Modern Applied Science*, vol. 3, no. 2, p. p3, 2009.

[10] Y. Ji, W. Xie, Y. Fan, Y. Shi, D. Kong, and J. Lu, "Degradation of trimethoprim by thermo-activated persulfate oxidation: reaction kinetics and transformation mechanisms," *Chemical Engineering Journal*, vol. 286, pp. 16–24, 2016.

[11] M. Malakootian, N. Olama, and M. Malakootian, A. Nasiri, "Photocatalytic degradation of metronidazole from aquatic solution by TiO_2-doped Fe^{3+} nano-photocatalyst," *International Journal of Environmental Science and Technology*, vol. 16, no. 8, pp. 4275–4284, 2019.

[12] Q. Cai and J. Hu, "Decomposition of sulfamethoxazole and trimethoprim by continuous UVA/LED/TiO_2 photocatalysis: decomposition pathways, residual antibacterial activity and toxicity," *Journal of Hazardous Materials*, vol. 323, pp. 527–536, 2017.

[13] I. Michael, E. Hapeshi, V. Osorio et al., "Solar photocatalytic treatment of trimethoprim in four environmental matrices at a pilot scale: transformation products and ecotoxicity evaluation," *Science of the Total Environment*, vol. 430, pp. 167–173, 2012.

[14] M. Klavarioti, D. Mantzavinos, and D. Kassinos, "Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes," *Environment International*, vol. 35, no. 2, pp. 402–417, 2009.

[15] M. Samarghandi, G. Asgari, S. Chavoshi, Z. Ghavami, and J. Mehralipour, "Performance of catalytic ozonation by Fe/MgO nanoparticle for degradation of cefazolin from aqueous environments," *Journal of Mazandaran University of Medical Sciences*, vol. 25, no. 128, pp. 77–90, 2015.

[16] A. Hassani, A. Khataee, S. Karaca, C. Karaca, and P. Gholami, "Sonocatalytic degradation of ciprofloxacin using synthesized TiO_2 nanoparticles on montmorillonite," *Ultrasonics Sonochemistry*, vol. 35, pp. 251–262, 2017.

[17] Y. Shi, Y. Zhang, Y. Cui et al., "Magnetite nanoparticles modified β-cyclodextrin polymercoupled with $KMnO_4$ oxidation for adsorption and degradation of acetaminophen," *Carbohydrate Polymers*, vol. 222, Article ID 114972, 2019.

[18] U. I. Gaya, A. H. Abdullah, M. Z. Hussein, and Z. Zainal, "Photocatalytic removal of 2, 4, 6-trichlorophenol from water exploiting commercial ZnO powder," *Desalination*, vol. 263, no. 1-3, pp. 176–182, 2010.

[19] Y. Huang, Y. Yang, J. Jiang, Z. Xu, C. Zhu, and L. Li, "Visible light photocatalytic ozonation of oxalic acid by MnOx-g-C3N4 composite," *Journal of Environmental Engineering*, vol. 144, no. 8, Article ID 04018063, 2018.

[20] M. Shabani, F. Essmaeil, A. Khoshfetrat, and D. Kahforoushan, "The application of ozonation process for the treatment of landfill leachate," *Journal of Civil and Environmental Engineering*, vol. 44, no. 76, pp. 39–45, 2014.

[21] Y. D. Shahamat, M. Farzadkia, S. Nasseri, A. H. Mahvi, M. Gholami, and A. Esrafili, "Magnetic heterogeneous catalytic ozonation: a new removal method for phenol in industrial wastewater," *Journal of Environmental Health Science & Engineering*, vol. 12, no. 1, p. 50, 2014.

[22] C. Baeza and D. R. U. Knappe, "Transformation kinetics of biochemically active compounds in low-pressure UV photolysis and UV/H_2O_2 advanced oxidation processes," *Water Research*, vol. 45, no. 15, pp. 4531–4543, 2011.

[23] C. Sirtori, A. Agüera, W. Gernjak, and S. Malato, "Effect of water-matrix composition on trimethoprim solar photodegradation kinetics and pathways," *Water Research*, vol. 44, no. 9, pp. 2735–2744, 2010.

[24] H. Bader, "Determination of ozone in water by the indigo method: a submitted standard method," *The Journal of the International Ozone Association*, vol. 4, no. 4, pp. 169–176, 1982.

[25] K. A. H. Buchan, D. J. Martin-Robichaud, and T. J. Benfey, "Measurement of dissolved ozone in sea water: a comparison of methods," *Aquacultural Engineering*, vol. 33, no. 3, pp. 225–231, 2005.

[26] N. Daneshvar, S. Aber, M. Seyeddorraji, A. Khataee, and M. Rasoulifard, "Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystalline ZnO powders under irradiation of UV-C light," *Separation and Purification Technology*, vol. 58, no. 1, pp. 91–98, 2007.

[27] M. H. Dehghani, B. Heibati, A. Asadi, I. Tyagi, S. Agarwal, and V. K. Gupta, "Reduction of noxious Cr (VI) ion to Cr (III) ion in aqueous solutions using H_2O_2 and UV/H_2O_2 systems," *Journal of Industrial and Engineering Chemistry*, vol. 33, pp. 197–200, 2016.

[28] T. Razavi, A. Fadaei, M. Sadeghi, and S. Shahsavan markadeh, "Study of the impact of combination of ZnO nanoparticles with ultraviolet radiation (photocatalytic process) on the removal of anionic surfactant linear alkyl benzene sulfonate (LAS) from aqueous solutions using taguchi statistical method," *Desalination and Water Treatment*, vol. 57, no. 59, pp. 28755–28761, 2016.

[29] M. Samarghandi, G. Asgari, S. Chavoshi, Z. Ghavami, and J. Mehralipour, "Performance of catalytic ozonation by Fe/MgO nanoparticle for degradation of cefazolin from aqueous environments," *Journal of Mazandaran University of Medical Sciences*, vol. 25, no. 128, pp. 77–90, 2015.

[30] W.-J. Huang, G.-C. Fang, and C.-C. Wang, "A nanometer-ZnO catalyst to enhance the ozonation of 2, 4, 6-trichlorophenol in water," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 260, no. 1, pp. 45–51, 2005.

[31] M. Abellán, J. Giménez, and S. Esplugas, "Photocatalytic degradation of antibiotics: the case of sulfamethoxazole and trimethoprim," *Catalysis Today*, vol. 144, no. 1-2, pp. 131–136, 2009.

[32] E. S. Elmolla and M. Chaudhuri, "Degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution by the UV/ZnO photocatalytic process," *Journal of Hazardous Materials*, vol. 173, no. 1-3, pp. 445–449, 2010.

[33] I. T. Peternel, N. Koprivanac, A. M. L. Božić, and H. M. Kusić, "Comparative study of UV/TiO_2, UV/ZnO and photo-fenton processes for the organic reactive dye degradation in aqueous

solution," *Journal of Hazardous Materials*, vol. 148, no. 1-2, pp. 477–484, 2007.

[34] T. Aissani, I. Yahiaoui, F. Boudrahem, S. Ait Chikh, F. Aissani-Benissad, and A. Amrane, "The combination of photocatalysis process (UV/TiO_2 (P25) and UV/ZnO) with activated sludge culture for the degradation of sulfamethazine," *Separation Science and Technology*, vol. 53, no. 9, pp. 1423–1433, 2018.

[35] G. Shankaraiah, S. Poodari, D. Bhagawan, V. Himabindu, and S. Vidyavathi, "Degradation of antibiotic norfloxacin in aqueous solution using advanced oxidation processes (AOPs)—a comparative study," *Desalination and Water Treatment*, vol. 57, no. 57, pp. 27804–27815, 2016.

[36] E. A. Serna-Galvis, J. Silva-Agredo, A. L. Giraldo, O. A. Flórez-Acosta, and R. A. Torres-Palma, "Comparative study of the effect of pharmaceutical additives on the elimination of antibiotic activity during the treatment of oxacillin in water by the photo-fenton, TiO_2 -photocatalysis and electrochemical processes," *Science of the Total Environment*, vol. 541, pp. 1431–1438, 2016.

[37] Q. Jiang, R. Zhu, Y. Zhu, and Q. Chen, "Efficient degradation of cefotaxime by a UV + ferrihydrite/TiO_2 + H_2O_2 process: the important role of ferrihydrite in transferring photo-generated electrons from TiO_2 to H_2O_2," *Journal of Chemical Technology & Biotechnology*, vol. 94, no. 8, pp. 2512–2521, 2019.

[38] M. Malakootian, H. Mahdizadeh, A. Dehdarirad, and M. Amiri Gharghani, "Photocatalytic ozonation degradation of ciprofloxacin using ZnO nanoparticles immobilized on the surface of stones," *Journal of Dispersion Science and Technology*, vol. 40, no. 6, pp. 846–854, 2019.

[39] S. Mustapha, M. Ndamitso, A. Abdulkareem et al., "Application of TiO_2 and ZnO nanoparticles immobilized on clay in wastewater treatment: a review," *Applied Water Science*, vol. 10, no. 1, pp. 1–36, 2020.

[40] M. Malakootian, A. Nasiri, A. N. Alibeigi, H. Mahdizadeh, and M. Amiri Gharaghani, "Synthesis and stabilization of ZnO nanoparticles on a glass plate to study the removal efficiency of acid red 18 by hybrid advanced oxidation process (ultraviolet/ZnO/ultrasonic)," *Desalination and Water Treatment*, vol. 170, pp. 325–336, 2019.

[41] M. Malakootian, M. Yaseri, and M. Faraji, "Removal of antibiotics from aqueous solutions by nanoparticles: a systematic review and meta-analysis," *Environmental Science and Pollution Research*, vol. 26, no. 9, pp. 8444–8458, 2019.

[42] A. Nasiri, F. Tamaddon, M. H. Mosslemin, M. Amiri Gharaghani, and A. Asadipour, "Magnetic nano-biocomposite $CuFe_2O_4$ @methylcellulose (MC) prepared as a new nano-photocatalyst for degradation of ciprofloxacin from aqueous solution," *Environmental Health Engineering and Management*, vol. 6, no. 1, pp. 41–51, 2019.

[43] S. Adhami, M. Fazlzadeh, and S. Hazrati, "Photocatalytic removal of cephalexin by UV/ZnO process from aqueous solutions," *Journal of Environmental Health Engineering*, vol. 5, no. 2, pp. 173–183, 2018.

[44] M. Malakootian, M. A. Gharaghani, A. Dehdarirad et al., "ZnO nanoparticles immobilized on the surface of stones to study the removal efficiency of 4-nitroaniline by the hybrid advanced oxidation process (UV/ZnO/O_3)," *Journal of Molecular Structure*, vol. 1176, pp. 766–776, 2019.

[45] S. Aghdasi and M. Shokri, "Photocatalytic degradation of ciprofloxacin in the presence of synthesized ZnO nanocatalyst: the effect of operational parameters," *Iranian Journal of Catalysis*, vol. 6, no. 5, pp. 481–487, 2016.

[46] M. Sadeghi, A. Mesdaghinia, A. Badkoobi, and R. Nabizadeh, "Enhancement of the biodegradability of methyl tert-butyl ether (MTBE) by advanced oxidation," *Water Wastewater*, vol. 58, pp. 54–61, 2005.

[47] B. Legube and N. K. V. Leitner, "Catalytic ozonation: a promising advanced oxidation technology for water treatment," *Catalysis Today*, vol. 53, no. 1, pp. 61–72, 1999.

[48] K. He, Y. M. Dong, Z. Li, L. Yin, A. M. Zhang, and Y. C. Zheng, "Catalytic ozonation of phenol in water with natural brucite and magnesia," *Journal of Hazardous Materials*, vol. 159, no. 2, pp. 587–592, 2008.

[49] Y. Dadban Shahamat, M. Farzadkia, S. Nasseri, A. H. Mahvi, M. Gholami, and A. Esrafily, "Evaluation of toxicity reduction, mineralization, and treatability of phenolic wastewater treated with combined system of catalytic ozonation process/biological reactor (SBR)," *Iranian Journal of Health & Environment*, vol. 8, no. 3, 2015.

[50] T. A. Ternes, J. Stüber, N. Herrmann et al., "Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater?" *Water Research*, vol. 37, no. 8, pp. 1976–1982, 2003.

[51] Y. Lester, D. Avisar, I. Gozlan, and H. Mamane, "Removal of pharmaceuticals using combination of UV/H_2O_2/O_3 advanced oxidation process," *Water Science and Technology*, vol. 64, no. 11, pp. 2230–2238, 2011.

[52] X. Zheng, S. Xu, Y. Wang, X. Sun, Y. Gao, and B. Gao, "Enhanced degradation of ciprofloxacin by graphitized mesoporous carbon (GMC)-TiO_2 nanocomposite: strong synergy of adsorption-photocatalysis and antibiotics degradation mechanism," *Journal of Colloid and Interface Science*, vol. 527, pp. 202–213, 2018.

[53] M. L. Tran, C.-C. Fu, and R.-S. Juang, "Effects of water matrix components on degradation efficiency and pathways of antibiotic metronidazole by UV/TiO_2 photocatalysis," *Journal of Molecular Liquids*, vol. 276, pp. 32–38, 2019.

[54] R. D. C. Soltani, M. Mashayekhi, M. Naderi, G. Boczkaj, S. Jorfi, and M. Safari, "Sonocatalytic degradation of tetracycline antibiotic using zinc oxide nanostructures loaded on nano-cellulose from waste straw as nanosonocatalyst," *Ultrasonics Sonochemistry*, vol. 55, pp. 117–124, 2019.

[55] N. Javid, Z. Honarmandrad, and M. Malakootian, "Ciprofloxacin removal from aqueous solutions by ozonation with calcium peroxide," *Desalination and Water Treatment*, vol. 174, pp. 178–185, 2020.